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Low Band Gap Planar Conjugated Pyrrole-Derived Polymers. Optical Absorbances From the UV  
to the Near-IR

by

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13. ABSTRACT (Maximum 200 words)  Described will be the synthesis of a pyrrole-derived polymer that can exist in a zwitterionic form ( $\lambda = 520$ nm), a partially reduced form ( $\lambda = 290$ nm), or a planar form ( $\lambda = 900$ nm). The absorptions are reversible depending on the pH of the medium.				
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Low Band Gap Planar Conjugated Pyrrole-Derived Polymers. Optical Absorbances From the UV to the Near-IR

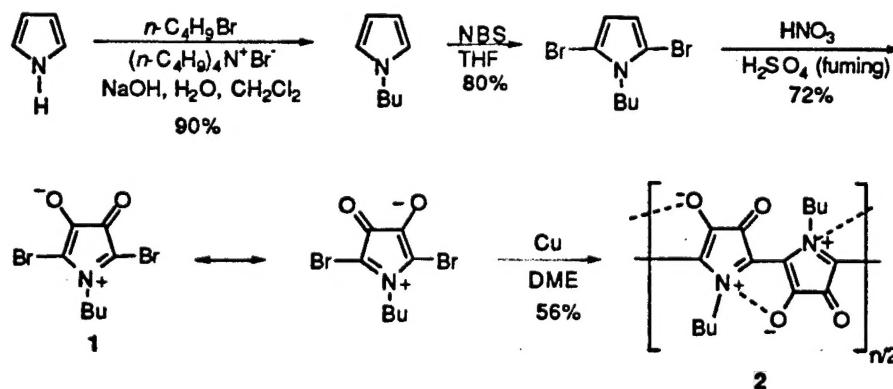
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In an effort to maximize the extended  $\pi$ -conjugation in polymers and to study their corresponding electronic and optical properties, several have undertaken the synthesis of new conjugated organic polymers that have a planar or near-planar conformation between the consecutive repeat units.<sup>1,2</sup> Described here is the synthesis of a unique zwitterionic pyrrole-derived polymer that can reversibly convert to a linear and planar conjugated polymer with a solution band gap of approximately 1.1 eV. The material possesses a reversible and enormous pH-dependent or solvent dependent absorption spectral range from the UV to the near-IR spectral region. Soluble polymeric materials that can respond dramatically and reversibly to external stimuli could have importance in the development of organic-based optical and electronic sensors,<sup>2</sup> while polymers with absorbances in the near-IR can serve as dyes for optical data discs.<sup>3</sup>

The synthesis of the new pyrrole-derived zwitterionic polymer is described in Scheme 1.

Scheme 1



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Pyrrole was N-alkylated under standard phase transfer conditions.<sup>4</sup> Bromination<sup>5</sup> and vigorous oxidation yielded the zwitterionic monomer **1**, a carbonyl-stabilized azomethine ylide, in an overall 52% yield for the three steps. The FTIR (KBr, 1718 cm<sup>-1</sup>, with no hydroxyl absorbance), mass spectrum (calc'd for C<sub>8</sub>H<sub>9</sub>Br<sub>2</sub>NO<sub>2</sub>: 311; found: 311), elemental analysis (calc'd: C, 30.89; H, 2.92; Br, 51.39; N, 4.50; found: C, 30.90; H, 2.92; Br, 51.25; N, 4.48), UV spectrum (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda$  = 248, 322; NMP,  $\lambda$  = 281, 320 (sh); there was little change in the UV spectra in the presence of aqueous NaOH or aqueous HCl), <sup>1</sup>H NMR [(300 MHz, CDCl<sub>3</sub>)  $\delta$  3.59 (t, J = 7.3 Hz, 2 H), 1.57 (p, J = 7.1 Hz, 2 H), 1.30 (sext, J = 7.3 Hz, 2 H), 0.91 (t, J = 7.3 Hz, 3 H)] and <sup>13</sup>C NMR [(75 MHz, CDCl<sub>3</sub>)  $\delta$  163.85, 129.24, 39.48, 30.39, 19.82, 13.52] were all consistent with the proposed structure. Note that two resonance forms exist for **1**, therefore there are only six peaks in the <sup>13</sup>C NMR spectrum.

We then sought to polymerize **1** using a variety of coupling methods.<sup>6</sup> (COD)<sub>2</sub>Ni(0),<sup>7</sup> copper(II) triflate,<sup>8</sup> and Rieke copper<sup>9</sup> failed to afford any polymeric product. Classical Ullman<sup>10</sup> coupling using copper-bronze (Aldrich) also failed when utilizing the common solvents (DMF, quinoline, tetramethylurea, or pyridine), however, in DME, copper-bronze-promoted polymerization (200°C, screw cap tube) of **1** afforded the desired polymer **2** (Scheme 1) in 56% yield after fractional precipitation (CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>OH). The precipitation dramatically sharpened the polydispersity (PD) to 1.15-1.25 with  $M_n$  = 3 130 (SEC, PS standards).<sup>11</sup> Spectral analysis again confirmed the proposed structure.

The optical spectra for **2** are most interesting. Polypyrrole has an absorption maximum of 420 nm (solid) but it is intractable. N-alkylated polypyrroles can be soluble, however, the increased steric repulsions between the consecutive aryl units causes a hypsochromic shift to approximately 380 nm.<sup>6</sup> Remarkably, the absorption maximum of **2** exhibits a strong bathochromically shifted absorbance that may be due to ionic interactions that force a diminution in the inter-unit twist angle as depicted in Scheme 1.<sup>2</sup> Solvatochromic effects are consistent with this proposal in that the following trend of S<sub>0</sub>-S<sub>1</sub> ( $\pi\pi^*$ )

absorption maxima are present for **2**:  $\text{CCl}_4$ , 520 nm; THF, 512 nm (Figure 1); EtOH/THF (1:1), 503 nm; acetone, 482

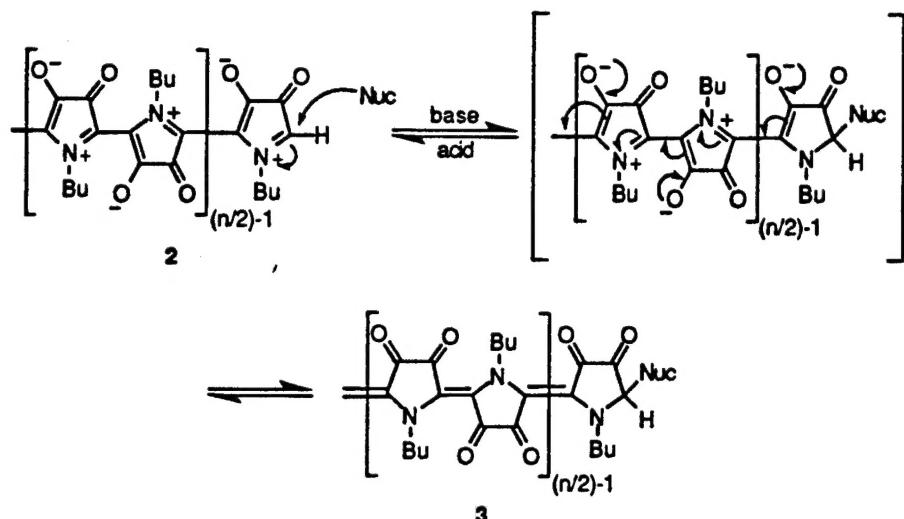
**Figure 1.** (a) Spectrum of **2** in THF (----). (b) Dissolution of **2** in THF/aqueous NaOH to form **3** (---).

nm. Thus when the charges can be solvent stabilized, inter-unit stabilization/planarization is retarded and the absorption shifts hypsochromically. Likewise, stabilization of the polar ground state increases the energy gap of the  $\pi-\pi^*$  transition which may exhibit charge transfer character.<sup>3,12</sup> Remarkably, when aqueous NaOH (0.05 M) was added dropwise to **2** in THF, the initial red-colored solution ( $\lambda_{\text{max}} = 512$  nm) became pale-orange and then finally brown ( $\lambda_{\text{max}} = 881$  nm) as more base was added (Figure 1). This pH-dependent shift in the absorption spectrum was reversible but polymer decomposition was detected after a few hours in the hydroxide-containing medium. Equally impressive solution effects occurred upon the dissolution of **2** in strongly Lewis basic solvents<sup>12</sup> such as HMPA ( $\lambda_{\text{max}} = 901$  nm) or NMP ( $\lambda_{\text{max}} = 746$  nm) (**2** was insoluble in DMSO) (Figure 2).<sup>13</sup> No polymer decomposition was

**Figure 2.** Dissolution of **2** in (a) HMPA (—) and (b) NMP (---).

detected in these Lewis basic solvents. Upon the addition of aqueous HCl, the HMPA and NMP solutions once again became red with no absorption bands present above 600 nm. The  $^{13}\text{C}$  NMR spectrum of **2** in HMPA (with 10%  $\text{CDCl}_3$  added for the lock) showed the butyl signals as well as a broad resonance from 176-163 ppm. In accord with the dramatic and reversible optical absorbance shifts, Brønsted or Lewis bases might be promoting a cascade of  $\pi$ -electron migrations in **2** to afford the planar conjugated polymer **3** (Scheme 2).

Scheme 2



Another interesting feature of **2** is that it could be partially reduced with H<sub>2</sub> (1 atm) over Pd/C (24 h, 23°C) to afford a system that is very similar to the starting polymer by FTIR, and SEC analysis, while the <sup>1</sup>H NMR and <sup>13</sup>C NMR showed peak broadening; therefore, some of the units were hydrogenated. Although the reduced polymer can not attain the degree of extended conjugation of **3** (as determined by the optical absorbances), its response range to different solvents can be from the UV region with weak tailing into visible, to the near-IR (DMSO,  $\lambda = 886$  nm) (Figure 3). Thus the reduced polymer is soluble in DMSO and it responds most dramatically to solvent changes.

**Figure 3.** Spectrum of the reduction product of **2**. (a) In THF (----) and (b) in DMSO (—).

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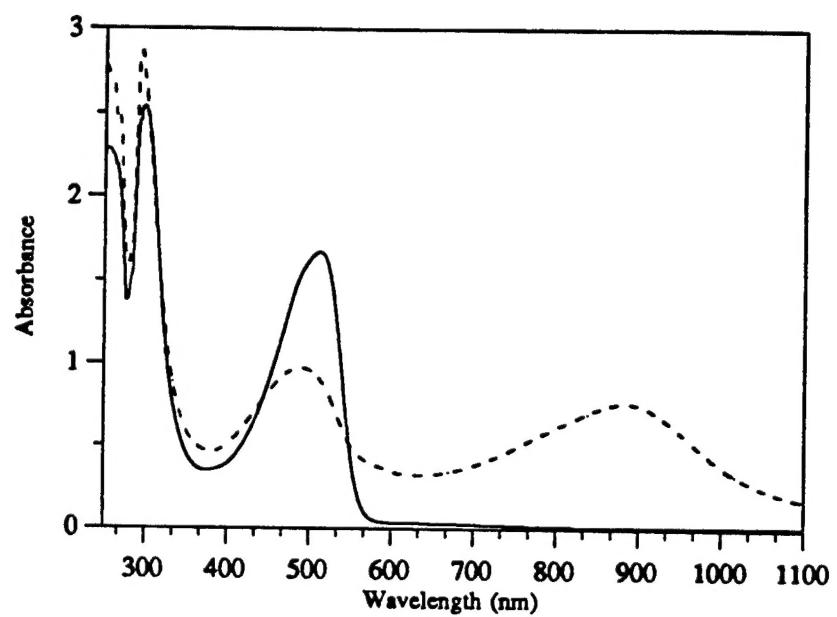


Fig 1

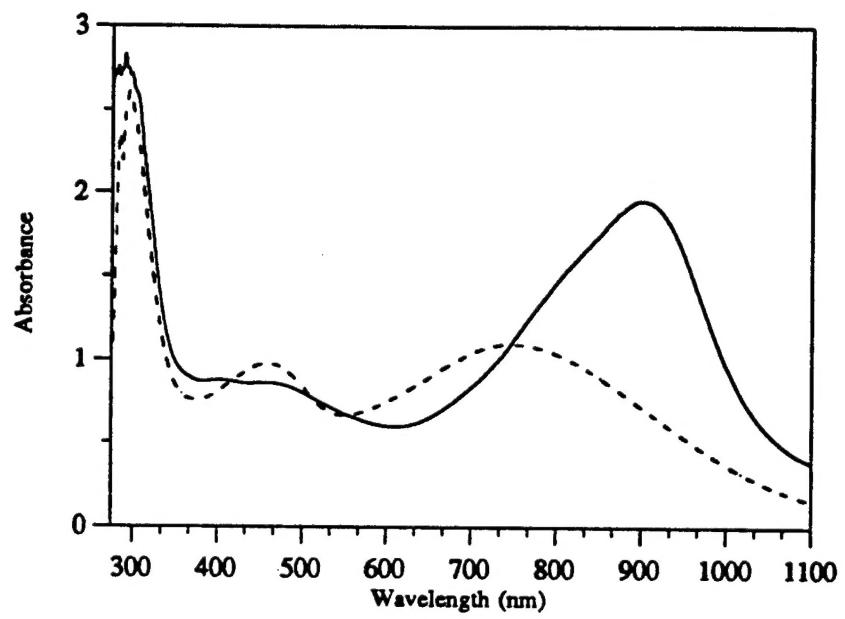


Fig 2

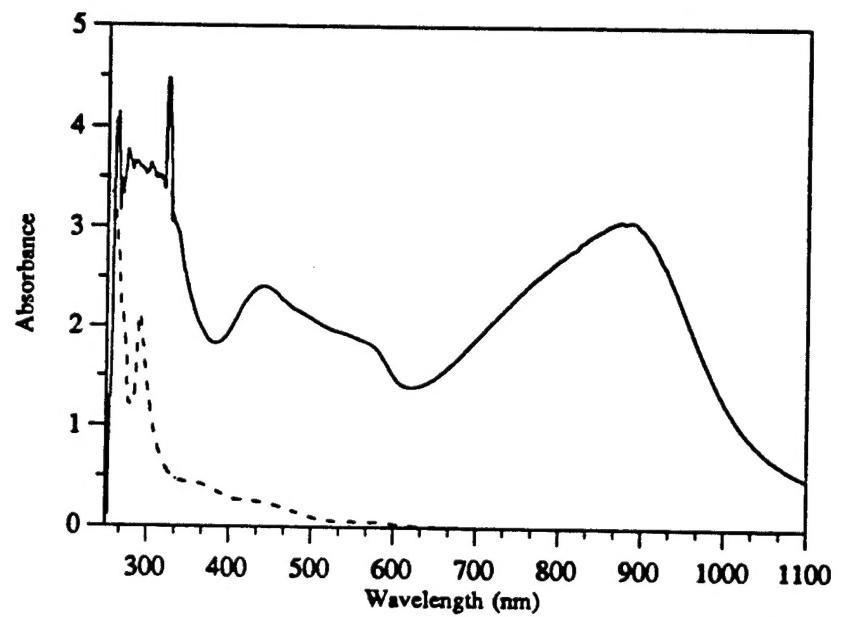


Fig 3